

Table I. Summary of QC Sample Analyses

Sample ID	Type	Theoretical Conc. ($\mu\text{g/L}$)	Soluble As ($\mu\text{g/L}$)	Recovery (%)
1-B-0	As+3	50	52	99
1-B-0	As+5	55	48	87
4-B-0	As+3	54	49	91
4-B-0	As+5	54	49	91
6-B-0	As+3	54	52	96
6-B-0	As+5	54	45	83

Table II. Summary of Wastewater Analyses

Sample ID	Soluble As ($\mu\text{g/L}$)	Arsenate As+5 ($\mu\text{g/L}$)	Arsenite As+3 ($\mu\text{g/L}$)
1-B-0	20	20	<5
2-B-0	19	19	<5
2-B-1	20	20	<5
2-B-2	510	271	239
2-B-3	<5	<5	<5
3-B-0	18	18	<5
4-B-0	19	19	<5
5-B-0	11	11	<5
5-B-1	11	11	<5
5-B-2	620	322	298
5-B-3	<5	<5	<5
6-B-0	17	16	<5
7-B-0	16	16	<5
7-B-1	13	13	<5
7-B-2	450	198	252
7-B-3	<5	<5	<5

Note: The instrument limit of quantitation (ILOQ) for total As (soluble As) was 5 $\mu\text{g/L}$. Since samples were not concentrated prior to analysis, the corresponding method limit of quantitation (MLOQ) was 5 $\mu\text{g/L}$. The ILOQ for As+5 and As+3 was 100 $\mu\text{g/L}$ As for each compound. However, since samples were concentrated 20x prior to analysis, the corresponding MLOQ was 5 $\mu\text{g/L}$ As.

V. Appendices

Appendix A
Analytical Method

EPL-BAS Project Number 251M01

Determination of Total Soluble Arsenic and Arsenic Species in Water using Graphite Furnace Atomic Absorption Techniques

Method Summary:

Water samples are filtered and diluted as necessary for analysis. Arsenic speciation analysis is performed using anion exchange HPLC with graphite furnace atomic absorption (GFAA) detection. Filtered samples are also analyzed by GFAA with Zeeman background correction for total soluble arsenic.

I. Standards, Reagents, and Solutions

A. Standards

Arsenic Reference Solution, Certified 1000 ppm, Fisher
Sodium Arsenite, Fisher Scientific, >99%
Sodium Arsenate, Fisher Scientific, 98.4%

B. Reagents

Ammonium Carbonate, Mallinckrodt
Nickel Nitrate Hexahydrate, Aldrich
Water, ASTM Type I

C. Solution Preparation

1. HPLC Eluent (0.2M ammonium carbonate)

Weigh 44 g ammonium carbonate into a 2 L volumetric flask and dilute to volume with Type I water. Store ambient.

2. Calibration Standard Solutions (for total As analysis)

Prepare standards in Type I water by appropriate dilution of the 1000 ppm As reference solution noted above. A concentration range of approximately 20 to 100 µg/L As should be prepared. Store standards frozen.

3. Reference Standard Solutions (for speciation analysis)

Dissolve appropriate amounts of sodium arsenite and sodium arsenate in Type I water. Store stock standards frozen. Prepare working reference standards by appropriate dilution of the stock solutions in Type I water. Store working standards frozen.

4. GFAA Matrix Modifier (0.4% Ni)

Weigh 2 g nickel nitrate hexahydrate into a 100 mL volumetric flask and dilute to volume with Type I water. Store ambient.

II. Equipment

Balances, Mettler, Sartorius, and American Scientific

Class A Glassware, acid-washed*

Atomic Absorption Spectrophotometer, Perkin-Elmer Model 460 equipped with an AS-1 Autosampler and HGA-2100 Graphite Furnace.

Atomic Absorption Spectrophotometer, Perkin-Elmer Zeeman 30/30 equipped with an AS-60 autosampler and HGA-600 Graphite Furnace.

Filters, 0.45 μ m Acrodiscs, Gelman

HPLC Pump, Perkin-Elmer Model 410

Arsenic Electrodeless Discharge Lamp, Perkin-Elmer

Switching Valve, Valco Instruments

LC Autosampler, Micromeritics

*All glassware and sample storage containers are soaked overnight and thoroughly washed with detergent and tap water, rinsed with water, and soaked for four hours in a mixture of dilute nitric and hydrochloric acid (1:2:9), followed by rinsing with ASTM Type I water and oven drying.

III. Methodology

A. Sample Preparation

1. Store water samples frozen upon receipt.
2. Filter a suitable aliquot of thawed water sample through a 0.45 μ m filter. Use the first 10-20 mL to rinse the filter and collect the remainder of the sample for analysis.
3. Prepare a QC spike at ca 20-50 μ g/L As for each; arsenite and arsenate, by addition of aqueous reference standard solutions to a water sample of known volume. A single QC spike is to be prepared and analyzed with each batch of water samples received.

B. Total Arsenic Analysis

Total soluble arsenic analysis is performed by GFAA with Zeeman background correction. Recommended analysis conditions are as follows.

Spectrometer: Wavelength: 193.7 nm
Slit: 0.7 nm
Lamp: Arsenic electrodeless discharge lamp
operated at ca 8 Watts.

Furnace Program: Dry Time: 30 seconds
Dry Temp: 120°C
Char Time: 30 seconds
Char Temp: 1300°C
Atomization Time: 5 seconds
Atomization Temp: 2350°C

Autosampler: Sample Injection Volume: 20 μ L
Matrix Modifier (0.4% Ni): 5 μ L

Calibration is performed by analysis of standards containing from ca 20 to 100 μ g/L elemental As.

C. Speciation Analysis

Speciation analysis is performed by anion exchange HPLC with GFAA detection. Recommended analysis conditions are as follows.

GFAA

Slit: 0.7 nm
Wavelength: 193.7 nm
Lamp: Arsenic electrodeless discharge lamp operated at ca 8
Watts
Dry Temp: 130°C
Dry Time: ca 20 seconds
Char Temp: 800°C
Char Time: ca 8 seconds
Atomization Temp: 2300°C
Atomization Time: 5 seconds
GFAA Autosampler Injection Volume: 10 μ L

HPLC

Solvent A
Solvent B

HPLC Water
0.2M $(\text{NH}_4)_2\text{CO}_3$

Column: 2 Brownlee Polypore AN (4.6 x 60 mm) anion exchange guard columns.

Solvent Program:

Time	% Solvent Flow (mL/minute)		Curve
Initial	100 A	0.5	—
20 minutes	100 B	0.5	1
30 minutes	100 A	2.0	1
44 minutes	100 A	0.5	—

Alternative HPLC Technique:

Column: 1 Alltech Universal Anion Exchange HPLC column (4.6 x 150 mm).

Solvent Program:

Time	% Solvent Flow (mL/minute)		Curve
Initial	100 A	0.5	—
30 minutes	65 A/35 B	0.5	1
40 minutes	100 B	0.5	1
50 minutes	100 A	2.0	1
52 minutes	100 A	0.5	—

Reference standards are analyzed to ascertain retention times for the inorganic arsenicals. Quantitation of each arsenical detected will be by cumulative peak height percent (see calculations).

IV. Calculations

A. Total Soluble As ($\mu\text{g/L}$) =

Analytical Result ($\mu\text{g/L}$) x Dilution Factor

B. Speciated As ($\mu\text{g/L As}$) =

Cumulative Peak Height Percent for Compound ____ x Total As ($\mu\text{g/L}$)

Where Peak Height Percent =

$$\frac{\text{Cumulative Peak Height for Compound}}{\text{Sum of Cumulative Peak Heights for all Compounds}}$$